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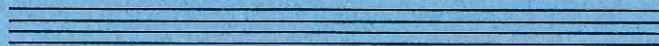
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THE
DEGRADATION OF PARACHUTES:
AGE AND MECHANICAL WEAR

By
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MAY 1992

FINAL REPORT
OCTOBER 1988 - SEPTEMBER 1990



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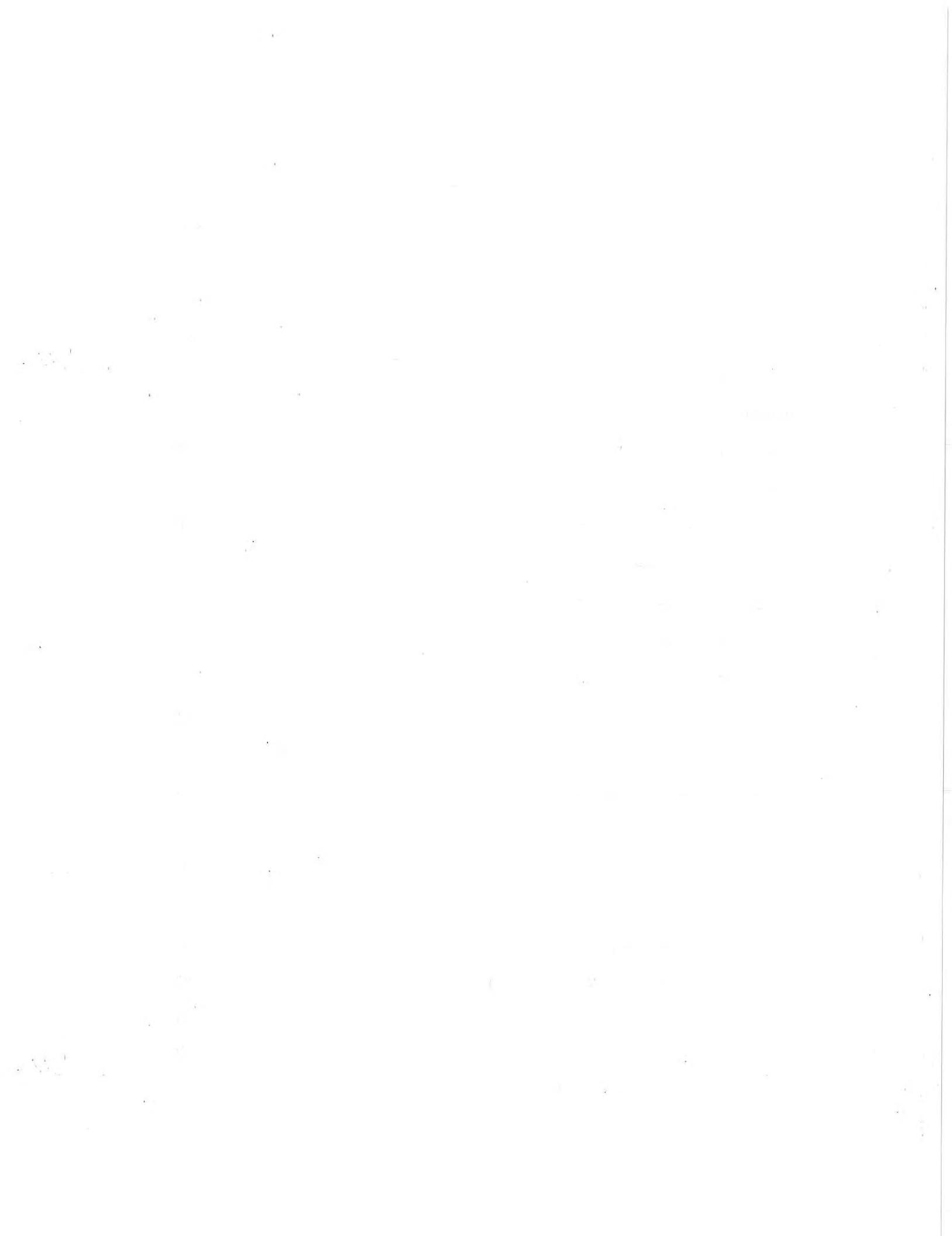
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Box 13 Abstract (Continued)

To answer the question of how storage life affects a parachute, it is recommended that: 1) the mechanical properties of the parachute materials at time of manufacture be determined and 2) more complete logs (number of jumps, dynamic load, jump terrain) be maintained throughout the life of the parachute.

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PREFACE

This work on the degradation of parachutes, or more specifically on the nylon 66 used in parachute suspension cord, was performed during the period October 1988 thru September 1990. It was funded under project number 1L162786D283AJ025 in Agg Code T/B1326 and was shared by the Physical Sciences Division and the Biological Sciences Division of the Soldier Science Directorate at Natick.

This technical report is submitted by the Materials Characterization Section of the Physical Sciences Division as our final report for this project and to fulfill our obligations to this work unit.

ACKNOWLEDGEMENT

The author is deeply indebted to Erwin A. Wuester for providing much highly relevant literature material and for his interesting and informative discussions of parachutes, their construction, storage and use and of the problems facing those charged with setting safe-use limits. The author is also greatly indebted to Bill Porter and Ed Black for providing the front-face fluorescence data, to Walter Yeomans for the mass spectral results and their interpretation and to Joseph Akkara for the UV/vis spectra.

INTRODUCTION

There has always been pressure to increase the shelf life and service life of parachutes, because extending the useful life of a parachute would save diminishing resources, reduce logistical support requirements and provide the field commander with greater flexibility in training and other necessary operations. Unfortunately, this pressure is being applied at the same time field commanders are increasing the jump loads, both static and dynamic (exit velocities), which puts greater stress on all parts of the parachute assembly. Parachute failure can lead to catastrophic results and no one can in good conscience grant such parachute life extensions without a considerable volume of good scientific data confirming that an extension is safe and reasonable.

The present study was undertaken to provide data that could be used to justify extending the shelf life of parachutes, i.e., to determine the effect of age on the degradation of nylon, particularly suspension cord, and to provide a means of determining the serviceability of parachutes. A second goal was to develop a nondestructive test method that could be used to evaluate parachutes and determine their serviceability at any time.

Initial plans called for the use of accelerated aging (high temperature storage) to produce changes in the nylon that could be easily measured by Instron testing and other physical and chemical means. This approach has been used by other researchers at both the Sandia Laboratories in the U.S. (1-5) and the Materials Research Laboratories in

Australia (8-12). A literature search employing DIALOG uncovered many research papers dealing with the degradation or loss of strength of nylon 66 as a function of age and other factors. More than 50 research articles were obtained including papers and technical reports from the Sandia labs (1-7), Australia (8-15), early in-house studies at the U.S. Army Natick RD&E Center going back more than 20 years (16-23), India (24-25), the El Centro parachute test facility in El Centro, CA (26) and the Wright Patterson Air Force Base (27,28). A study of these papers indicated that the use of accelerated aging might not provide the reliability that was needed and that the literature data themselves might be the best source of information that could be obtained within reasonable time frames.

Accelerated aging (storage at high temperatures) is considered an unreliable method for studying the factors that cause nylon degradation because in the one case of prime interest, the effect of humidity, it is clear that high temperature aging provides results in direct conflict with data obtained at normal temperatures (4,5,16). Accelerated aging requires the assumption that the mechanism producing the change in nylon is a first-order reaction so that the data obtained at high temperatures can be related to changes that would occur at ambient temperatures by the Arrhenius equation. Apparently the mechanism involving moisture does not follow this rule, or, at least when acting in concert with other factors, the result is not first order. This fact suggests that accelerated aging should not be used unless the reaction kinetics are well understood.

One of the factors that is known to affect the degradation rate of nylon is ultraviolet light. However, for stored parachutes this can be readily controlled by proper conditions. Dyes also have an effect on the

degradation of nylon but in the case of the suspension cord, which is the focus of the present report, the inner strands are undyed and should not be greatly affected by the dye in the outer sheath. The nylon also contains UV inhibitors. These would tend to slow reactions at the beginning of storage and after their depletion allow the degradation to proceed at its normal rate. This behavior could not be detected using accelerated storage. Other factors that cause degradation of nylon include overloads, the number of strain cycles (mechanical work-in), dirt, particularly the kind of grit or sand that might penetrate into the suspension cord, and moisture, especially salt water that could leave residual salt crystals in the parachute cord. These factors have not been considered in this report other than their combined effect on the used parachutes studied.

Very little data were obtained on parachutes or nylon 66 that had been stored for long periods of time. One study from India (24) reported on nylon canopy material that was placed in controlled storage and withdrawn for testing each year for a total of nine years. These data are included in this report, even though it was obtained on canopy material, because it is one of only two long-term storage studies obtained. The other long-term storage data come from an in-house report (16) where parachute material, including cord, was placed into storage under four different climatic conditions and evaluated after eight years. Data for the interim years were not obtained because of funding limitations.

The bulk of the data included in this report comes from studies on used parachutes. The concentration has been on the parachute suspension cord. Data from a Natick Technical Report resulting from a contract with

Albany International (20) and a recent internal study (two memos for Chief, PEB, AMED, ATTN: E. Wuester, dated 19 Jan 90 and 22 Feb 90) on parachutes that were received from the 1989 "Just Cause" exercise provide all the data on the overall degradation due to the combined effects of age and use. These data in combination with other internal reports allowed the separation of degradation into the use-dependent part and the age-dependent part. Fluorescence data, UV/vis spectra and mass spectrometric results were also obtained and support conclusions drawn from the test data on the used parachutes.

METHOD AND DATA ANALYSIS

GENERAL: Most of the data included in this report were obtained on used parachutes and in many cases the tests were conducted in-house or under contracts initiated by Natick. For most of the parachutes evaluated only the date of manufacture and the date the parachute was placed in service are known. For one group of parachutes obtained from the U.S. Forestry Service, the number of times the parachute had been jumped was also known. From this information the author has tried to extract the changes in the nylon that can be attributed to the normal aging of the nylon itself.

LITERATURE DATA: Figure 1 shows the tensile strength data obtained from the literature on the suspension cord from used parachutes. Sixty-two parachutes were evaluated and described in the Albany International report (20) and 30 parachutes from the "Just Cause" exercise were recently evaluated in-house. Also included in Fig. 1 are the results from limited

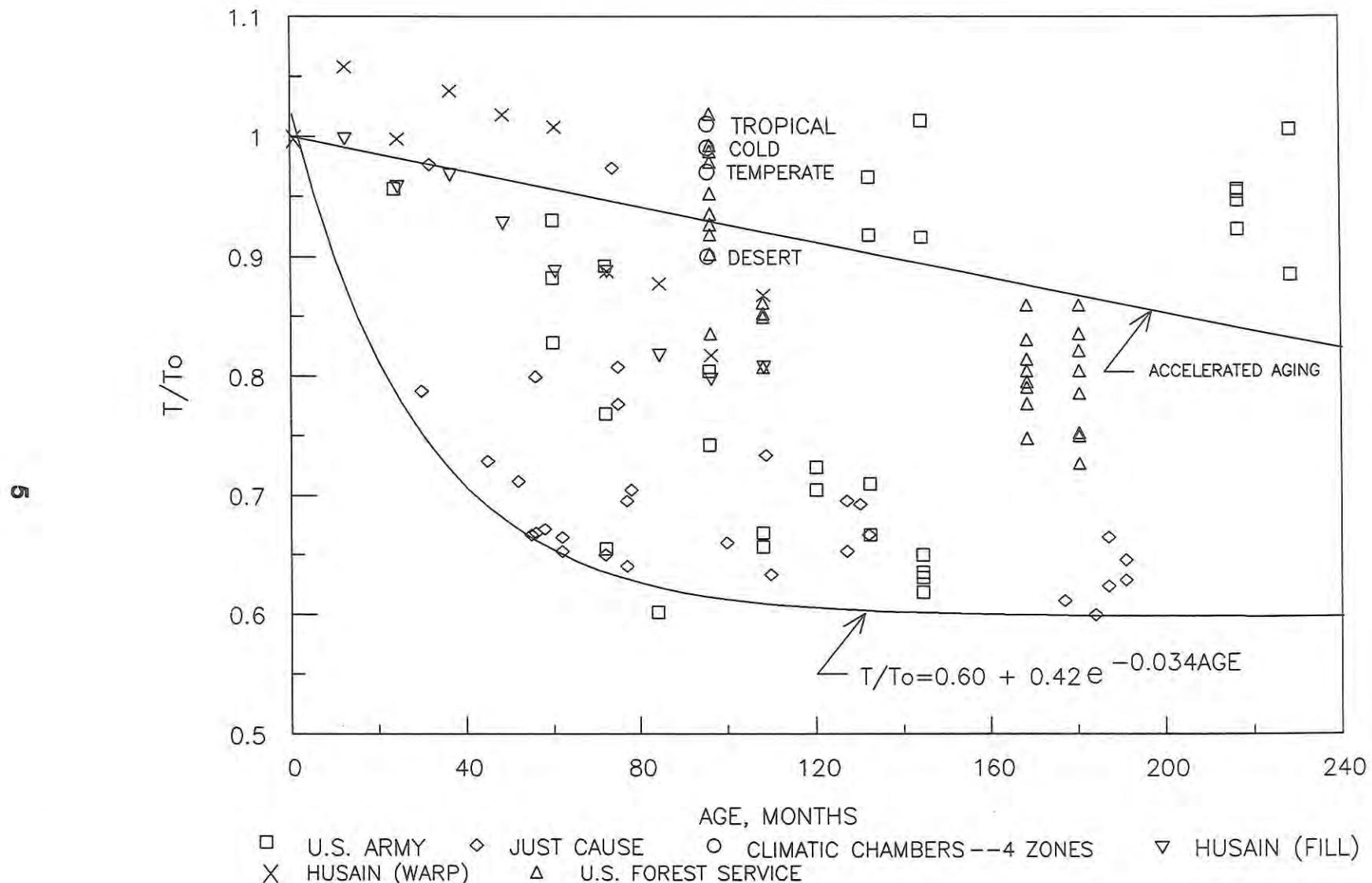


Figure 1. Plot of the normalized tensile strength (T/T_0) vs age for data found in the literature.

studies on unused canopy material, unused suspension cord and accelerated aging. This plot gives the reduced tensile strength T/T_0 as a function of the age (from date of manufacture) of the parachute. The reduced tensile strength is the breaking strength as measured in an Instron tensile test divided by a reasonable estimate of the average strength of the cord when it was in its pristine condition. This estimated value was taken as the minimum strength allowed by the specification in effect at the time of manufacture plus 5 percent. For all parachutes included in Fig. 1 the minimum allowed strength is 400 lb (181.4 kg), thus T_0 is 420 lb (190.5 kg). Also included in Fig. 1 are data (4-points) obtained on parachute material stored in the Natick climatic chambers for eight years (16). There is one data point for each of four climatic storage conditions 1) tropical (high temperature, high humidity; 2)desert (high temperature, low humidity; 3)temperate summer (moderate temperature, moderate humidity); 4)arctic (cold, low humidity). Figure 1 shows one set of data (Husain) for unused canopy material (24). This material was placed in storage and evaluated each year for a nine-year period; data for both the warp and fill directions are shown. Also included in the plot is a straight line which represents the results of accelerated aging studies undertaken in Australia (9,12). The line gives the degradation rate of nylon 66 canopy material extrapolated to 25°C from data obtained at higher temperatures. Also included in the figure is a curve which represents the worst case scenario for all the parachutes included in this report. All but one of the 92 used parachutes included in this report lie above this line; all of the data for unused material lie far above this line. The one point falling outside this boundary lies very close to it.

This line is simply an exponential decay curve, generated by arbitrarily choosing parameters that place the curve close to the lower boundary of all the data points.

Some of the data included in the Albany International report (20) were obtained on parachutes used by the U.S. Forestry Service. The history of these parachutes was more complete and the number of jumps each parachute had sustained was known. For this group of 32 parachutes it is possible to investigate the effect of the number of jumps on the tensile strength of the parachute suspension cord. Figure 2 shows the reduced tensile strength plotted against the number of jumps; the line through the data is the result of a nonlinear (quadratic) regression analysis. The R^2 value for this curve is 0.718. These data points were also fitted to both a linear regression and a multiple linear regression where the second independent variable was the age of the parachute. R^2 for the linear fit was 0.636 and for the multiple regression R^2 was 0.640. Including the age of the parachute in the regression analysis did not improve the degree of fit. The multiple regression equation

$$T/T_0 = 0.997 - 0.00292(\text{jumps}) - 0.00038(\text{age})$$

shows that age contributes only 1/10 as much as the number of jumps. This is also shown in Fig. 3 where the tensile strength based on (1) the quadratic fit and (2) the multiple regression is plotted versus the actual tensile strengths. There is virtually no difference between the two data sets.

FLUORESCENCE MEASUREMENTS: Previous researchers had shown a strong correlation between the tensile strength of nylon 66 and its optical absorbance at 245 nm (1,2). However, the nylon used in these tests had

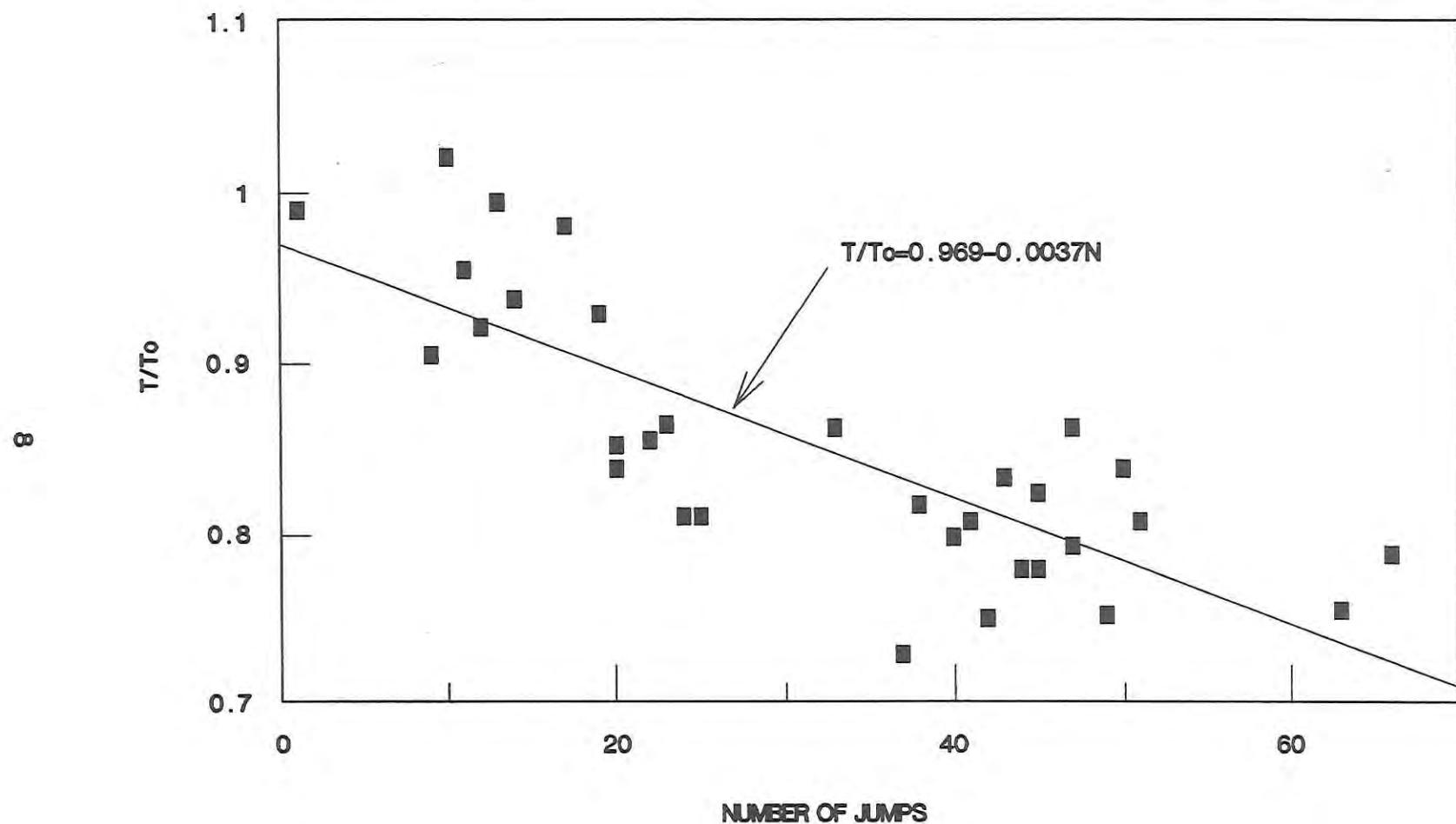


Figure 2. Normalized tensile strength vs number of jumps for U.S. Forestry parachutes. Curve represents the linear least squares fit.

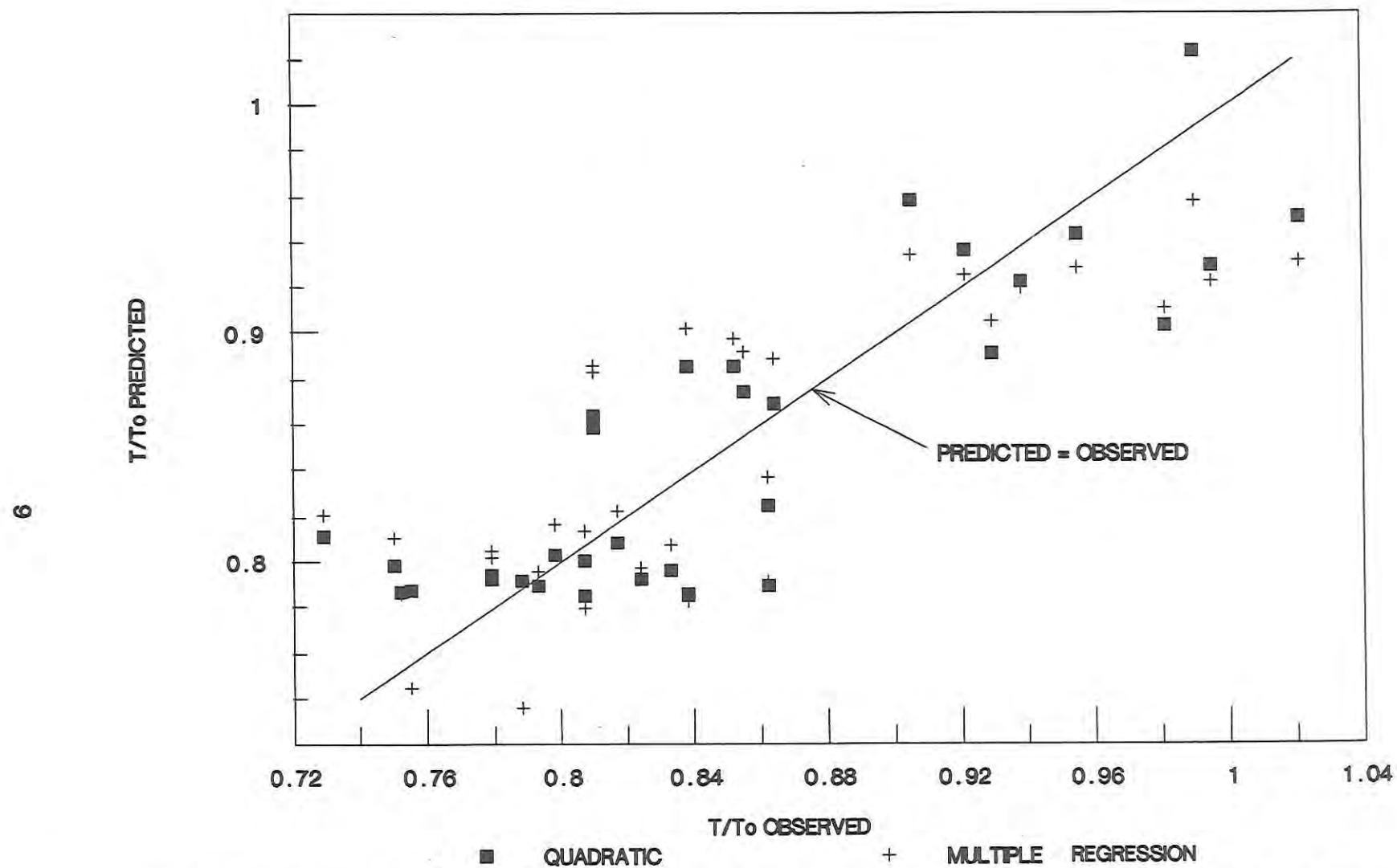


Figure 3. Predicted T/To vs the observed T/To for data of Fig. 2. Predictions using both a quadratic fit to the data of Fig. 2 and a linear multiple regression using age and number of jumps as independent parameters are shown.

been artificially aged using elevated temperatures, often above the glass transition of the nylon. One goal of this study was to determine whether or not fluorescence could be used to evaluate the serviceability of stored parachutes, i.e., can fluorescence measurements detect changes in nylon 66 that occur upon normal storage.

In previous studies the researchers dissolved the nylon and made their fluorescence measurements on the polymer solution. In this work the nylon thread from the center of the parachute cord was tightly wrapped on a glass microscope slide and taped in position. The slide was then placed in a Spex Fluorolog spectrophotometer for front-face fluorescence measurements. The instrument was operated in two different modes. First the excitation wavelength was set at 360 nm and the emitted light was monitored. The intensity of the scattered light, the intensity at the maximum of the emitted light and the wavelength at this maximum were recorded. This procedure was repeated for an excitation wavelength of 395 nm. In the second mode, the emitted light was monitored at only 470 nm while the excitation wavelength was varied. The excitation frequency that produced the greatest emission and the intensity of that emitted light were recorded. From these measured quantities three parameters were obtained to characterize the material. The first was the ratio of the maximum intensity to the scattered intensity for excitation at 360 nm. The second parameter was the ratio of the maximum intensity at an excitation of 395 nm to the maximum intensity at an excitation of 360 nm. The third parameter was the ratio of light emitted at 470 nm when excited at 395 nm to the light emitted at 470 nm when excited at 370 nm. These

parameters were self calibrating in that the absolute intensity of the excitation signal was not required.

Figures 4, 5 and 6 show the fluorescence parameters plotted against the age of the parachutes. Only the ratio of the maximum intensity to the scattered intensity (Fig. 4) shows any correlation. Figures 7,8 and 9 show the same fluorescence parameters plotted against the reduced tensile strength of the parachutes; none of the fluorescence measures correlate with the tensile strength.

MASS SPECTRAL RESULTS: In addition to the fluorescence measurements, several suspension cord samples from the same parachutes that were used for fluorescence measurements were subjected to chemical analysis using a Finnigan model 4500 GC/MS mass spectrometer. The undyed thread from the core of the suspension cords was pyrolyzed in the instrument and the vapors analyzed for molecular weight distributions. Three of the more prominent peaks were selected to characterize the parachute suspension cords. The magnitudes of these peaks are plotted against the age of the parachute cord in Figs. 10, 11 and 12 and against the tensile strength of the parachute cord in Figs. 13, 14 and 15.

UV/VIS SPECTRA: Selected nylon suspension cord samples were cut into 2 cm lengths. The inner core was separated from the outer sheath of the cord and the two parts were treated as separate samples.

Samples of the inner core and the outer sheath of nylon parachute suspension cord were accurately weighed to 0.1 mg and introduced into a 4 mL high performance liquid chromatography (HPLC) vial and sealed with a teflon septum. The nylon samples were solubilized in trifluoroethanol (Aldrich Chemicals, Inc.). The final concentration of nylon was in the

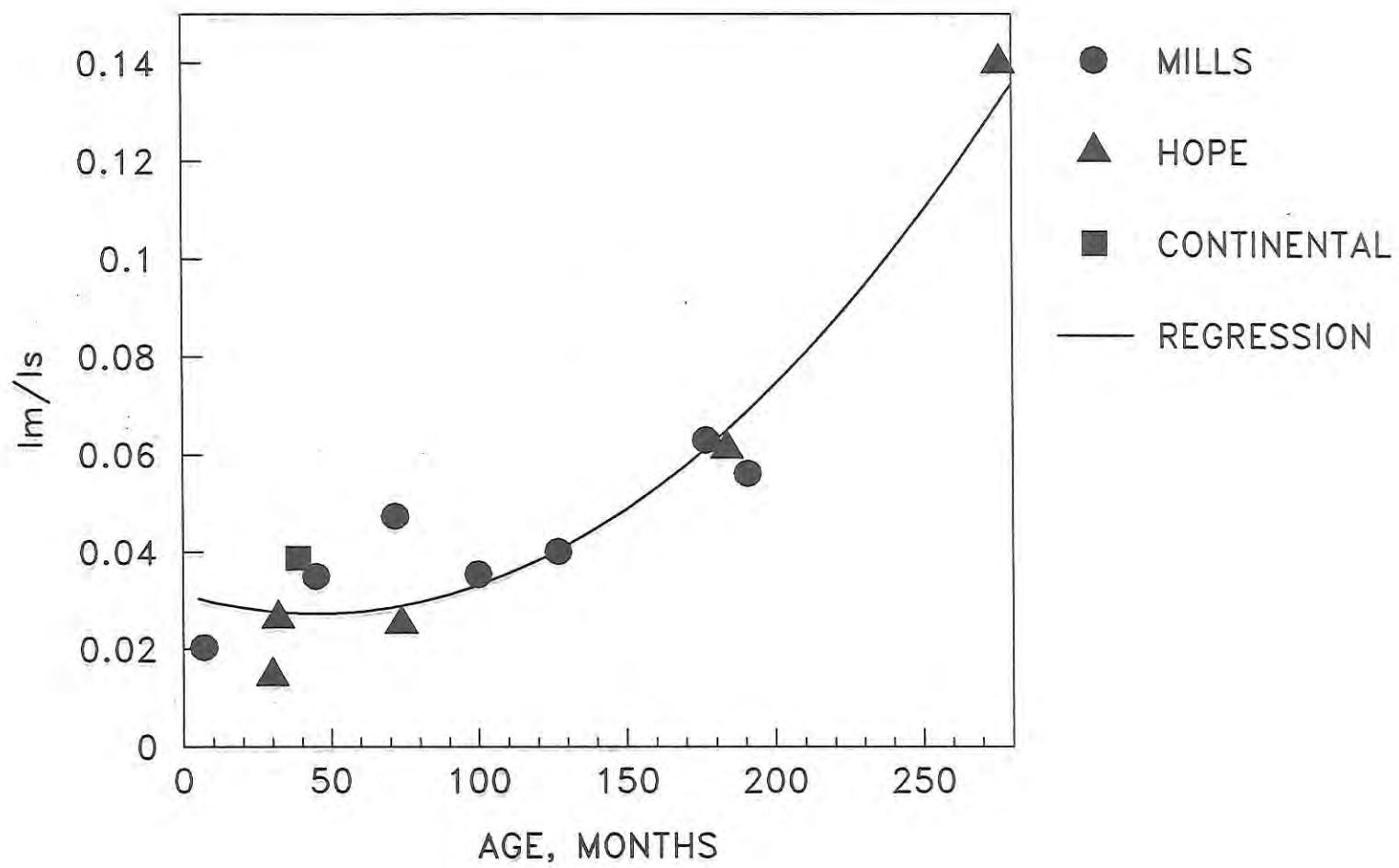


Figure 4. Fluorescence parameter maximum intensity/scattered intensity vs age of the parachute. Data for parachute cord manufactured by Mitex Industries Inc. (MILLS); Hope Webbing Co. (HOPE); Continental Cordage Corp. (CONTINENTAL) are shown.

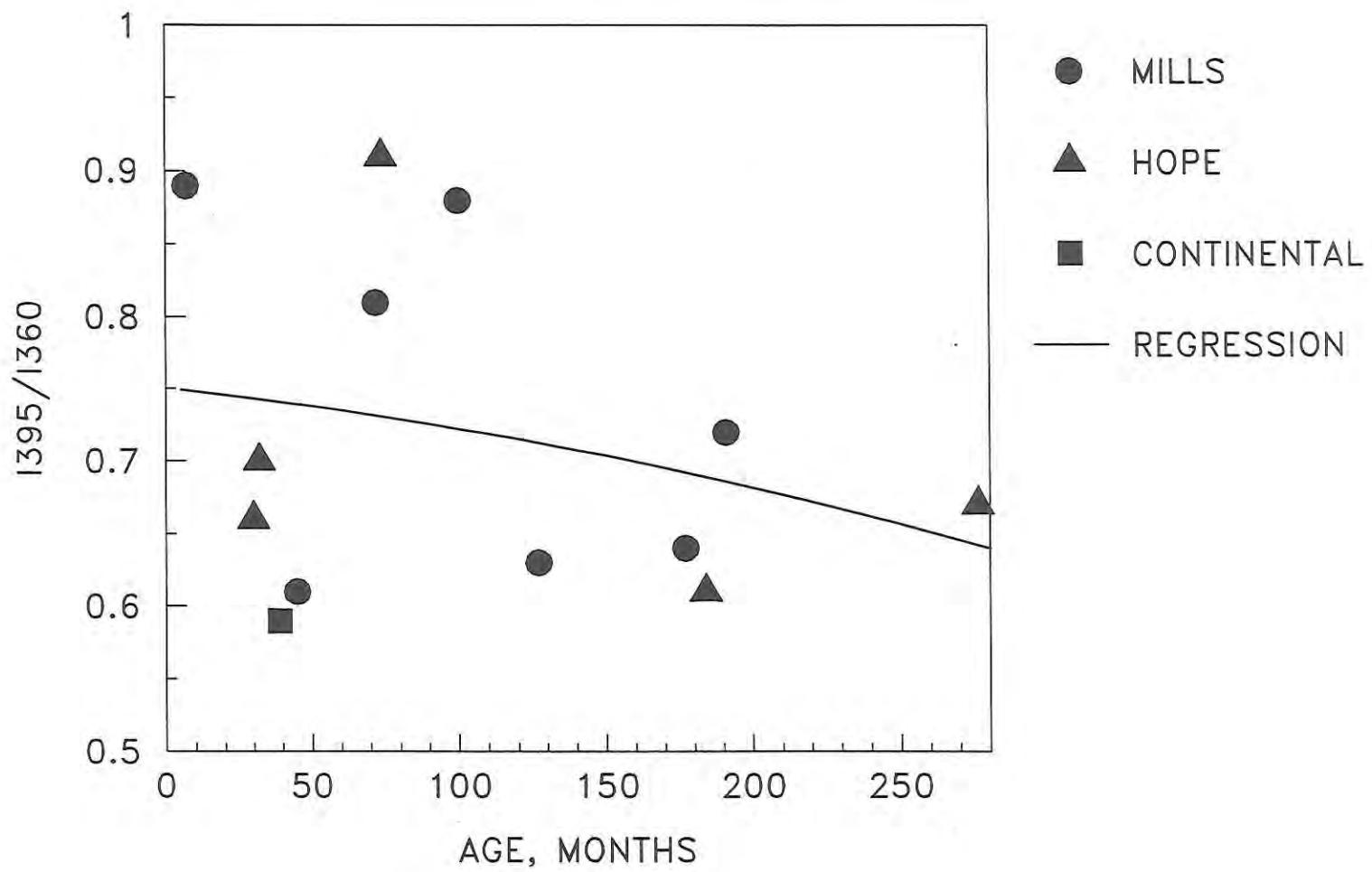


Figure 5. Fluorescence parameter $I395/I360$ vs age of the parachute. Symbols same as in Fig. 4.

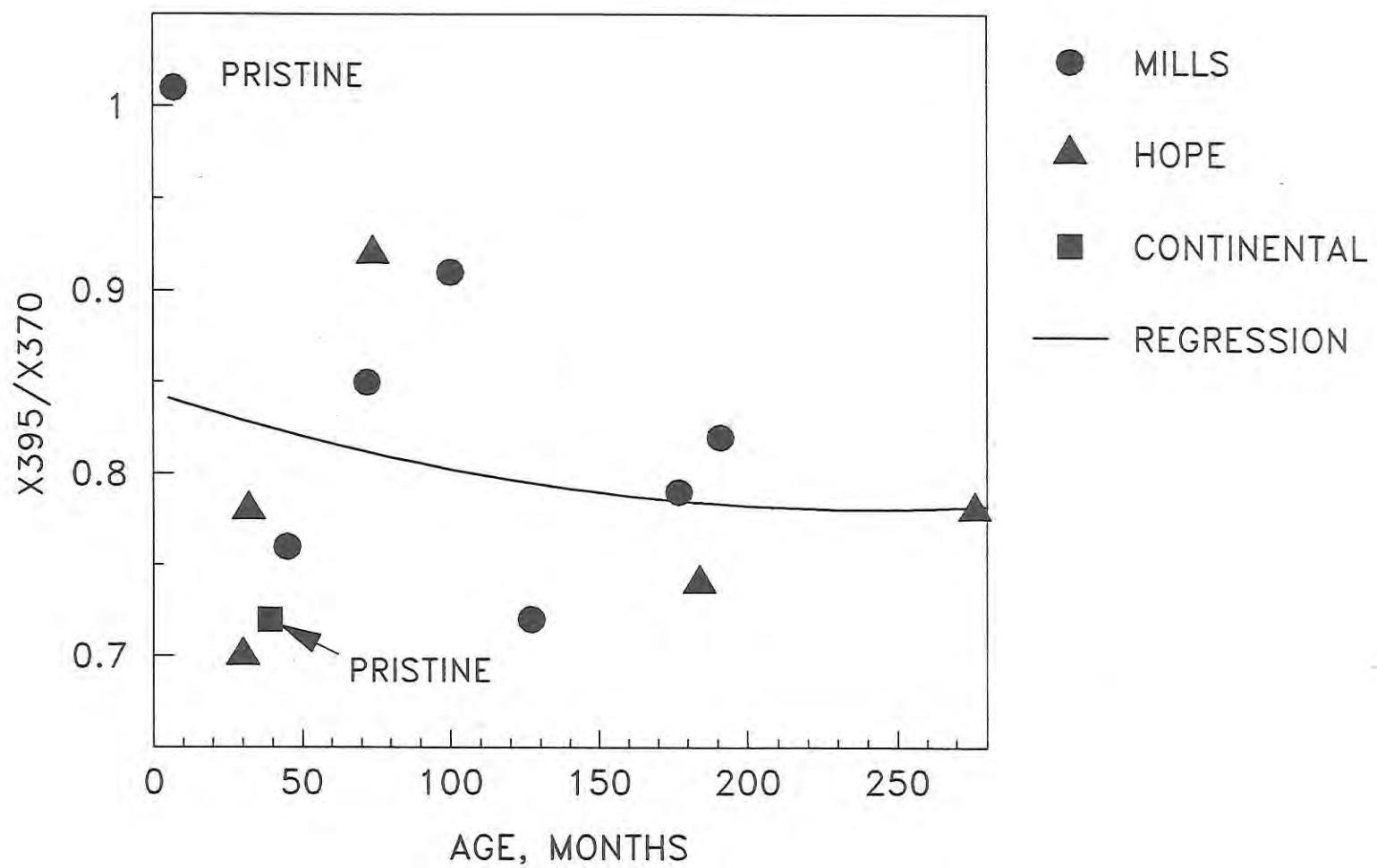


Figure 6. Fluorescence parameter $X395/X370$ vs age of the parachute. Symbols same as in Fig. 4.

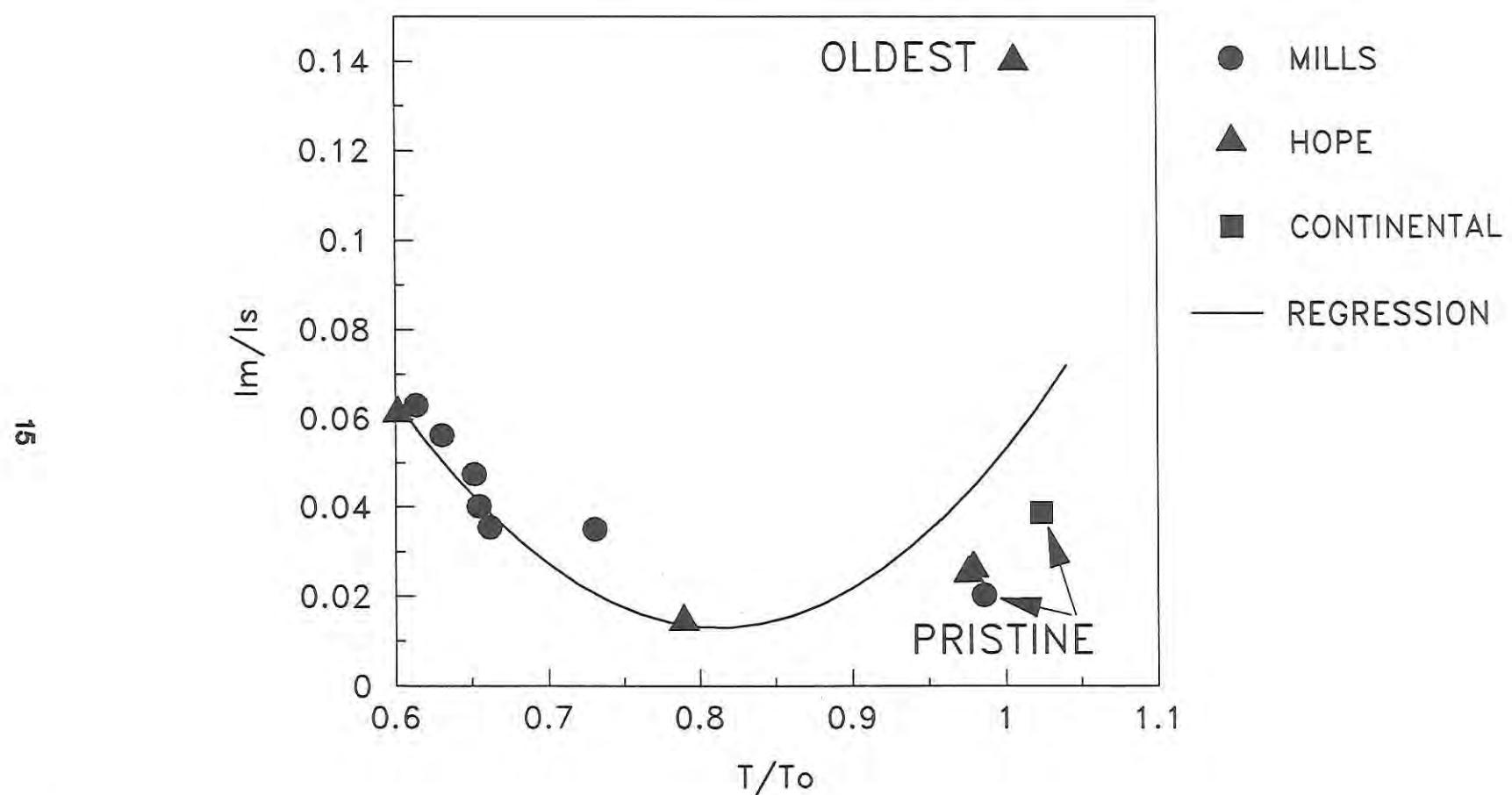


Figure 7. Fluorescence parameter Im/Is vs reduced tensile strength. Symbols same as in Fig. 4.

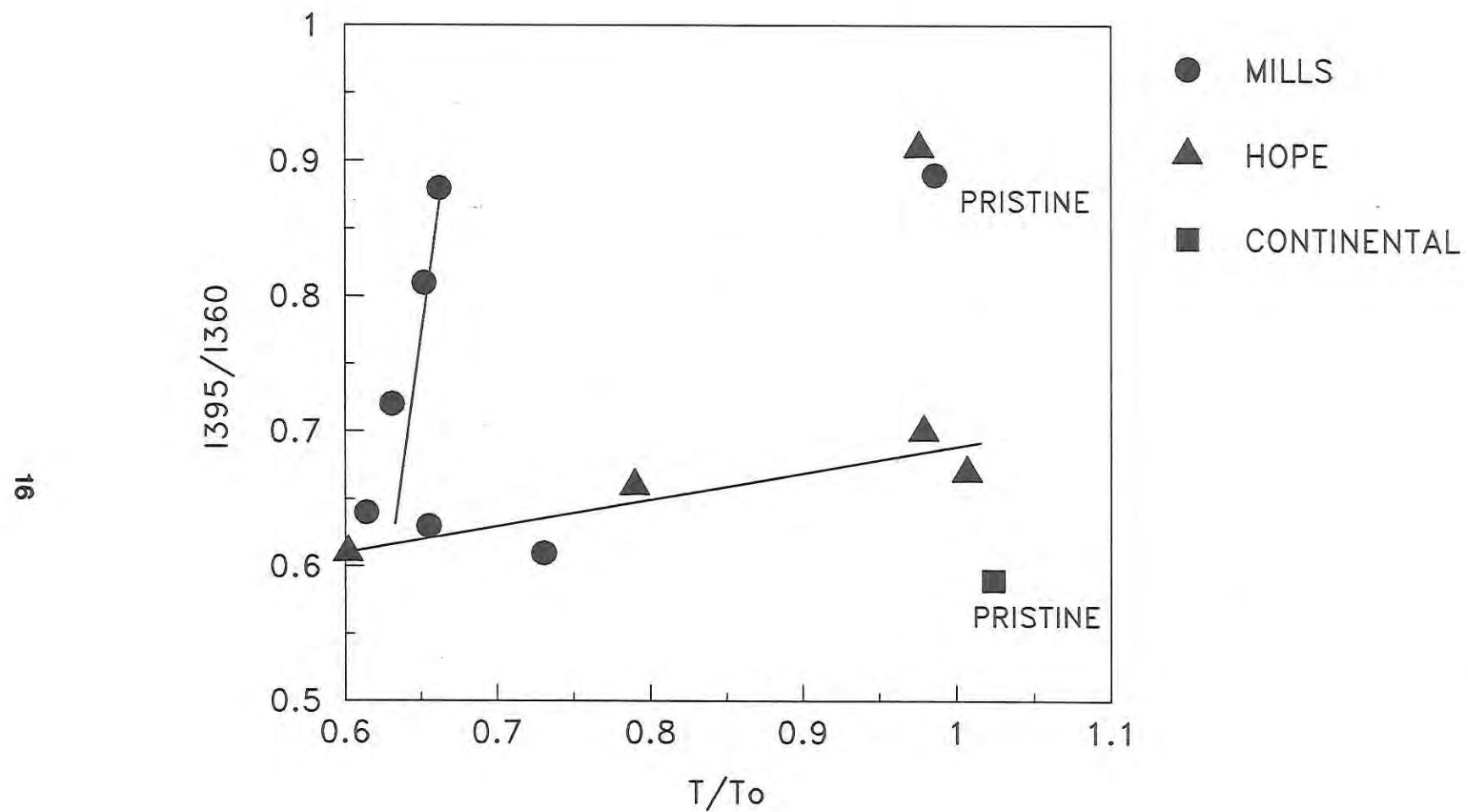


Figure 8. Fluorescence parameter I_{395}/I_{360} vs reduced tensile strength. Symbols same as in Fig. 4.

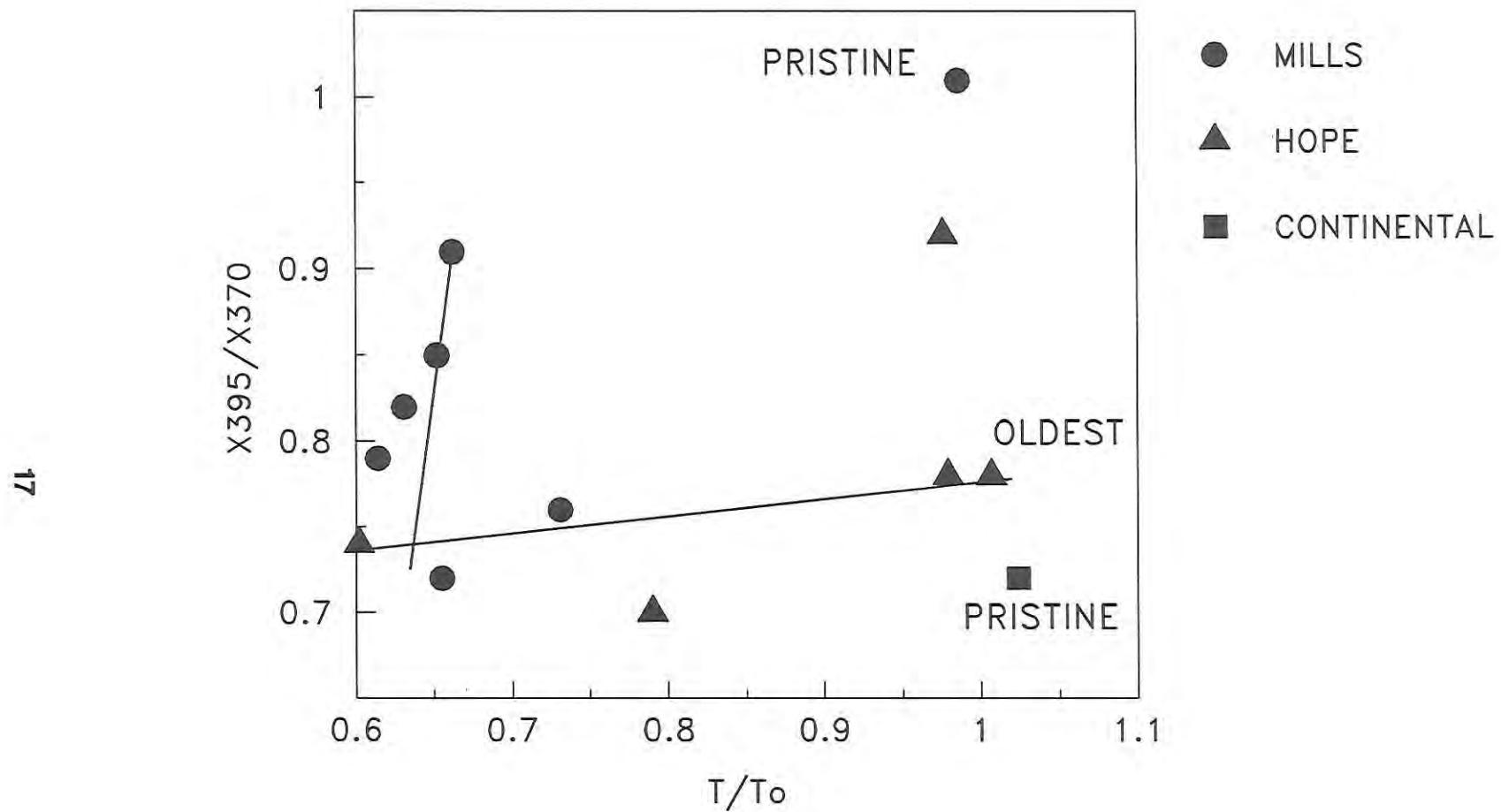


Figure 9. Fluorescence parameter X_{395}/X_{370} vs reduced tensile strength. Symbols same as in Fig. 4.

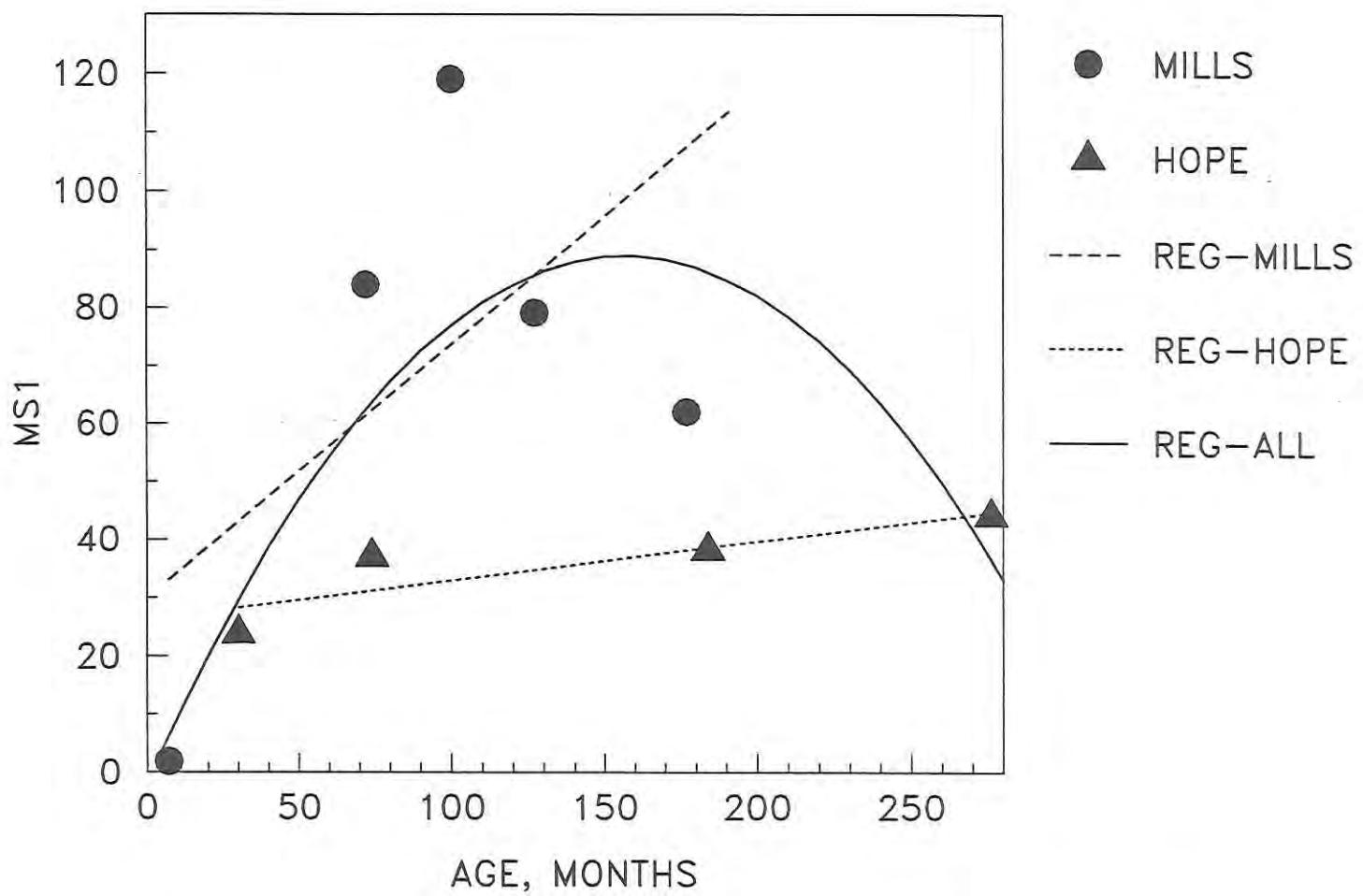


Figure 10. Mass Spectral parameter MS1 vs age of the parachute. Symbols same as in Fig. 4.
The parachute made by Continental was not evaluated.

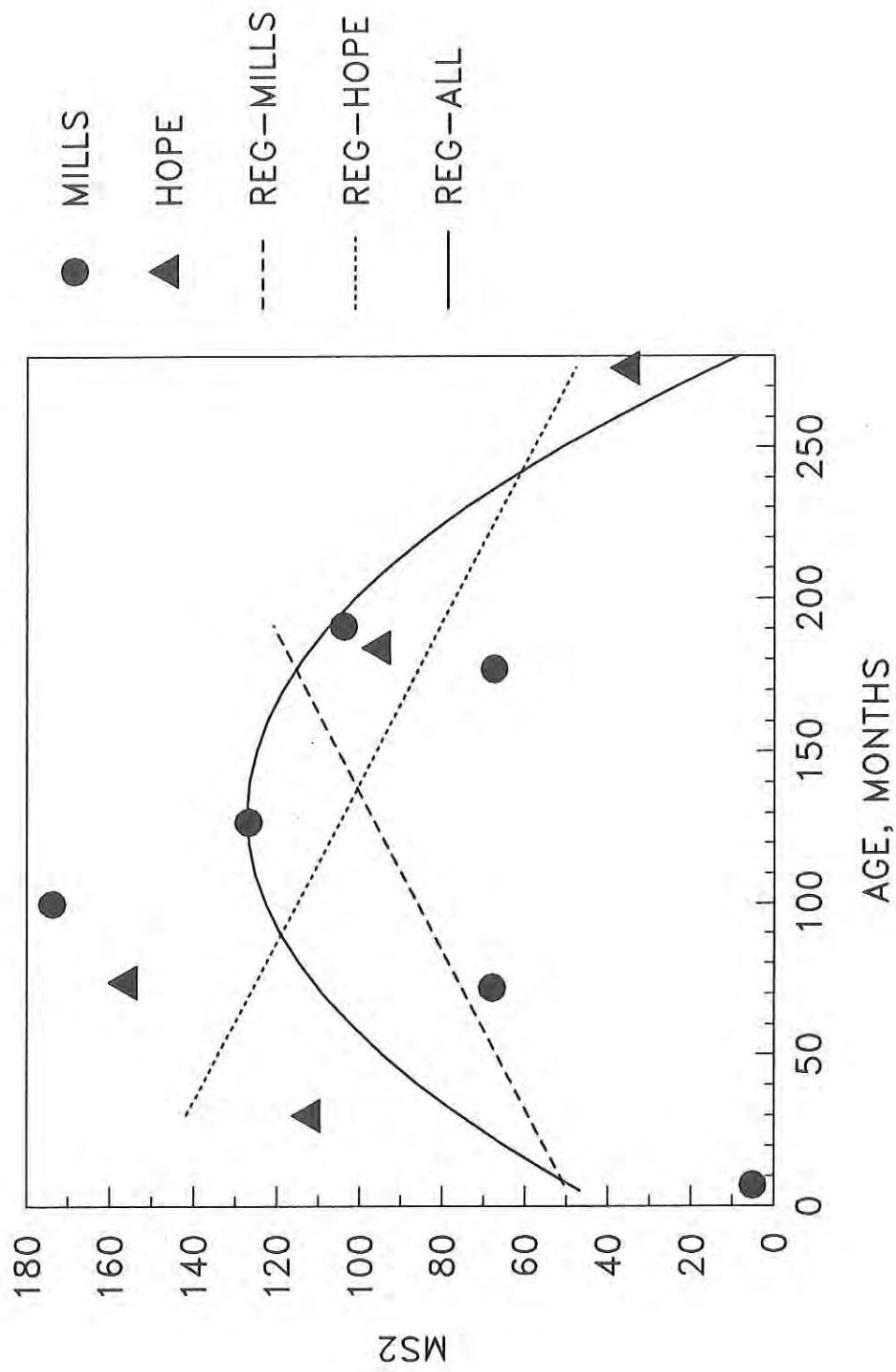


Figure 11. Mass Spectral parameter MS2 vs age of the parachute. Symbols same as in Fig. 4.

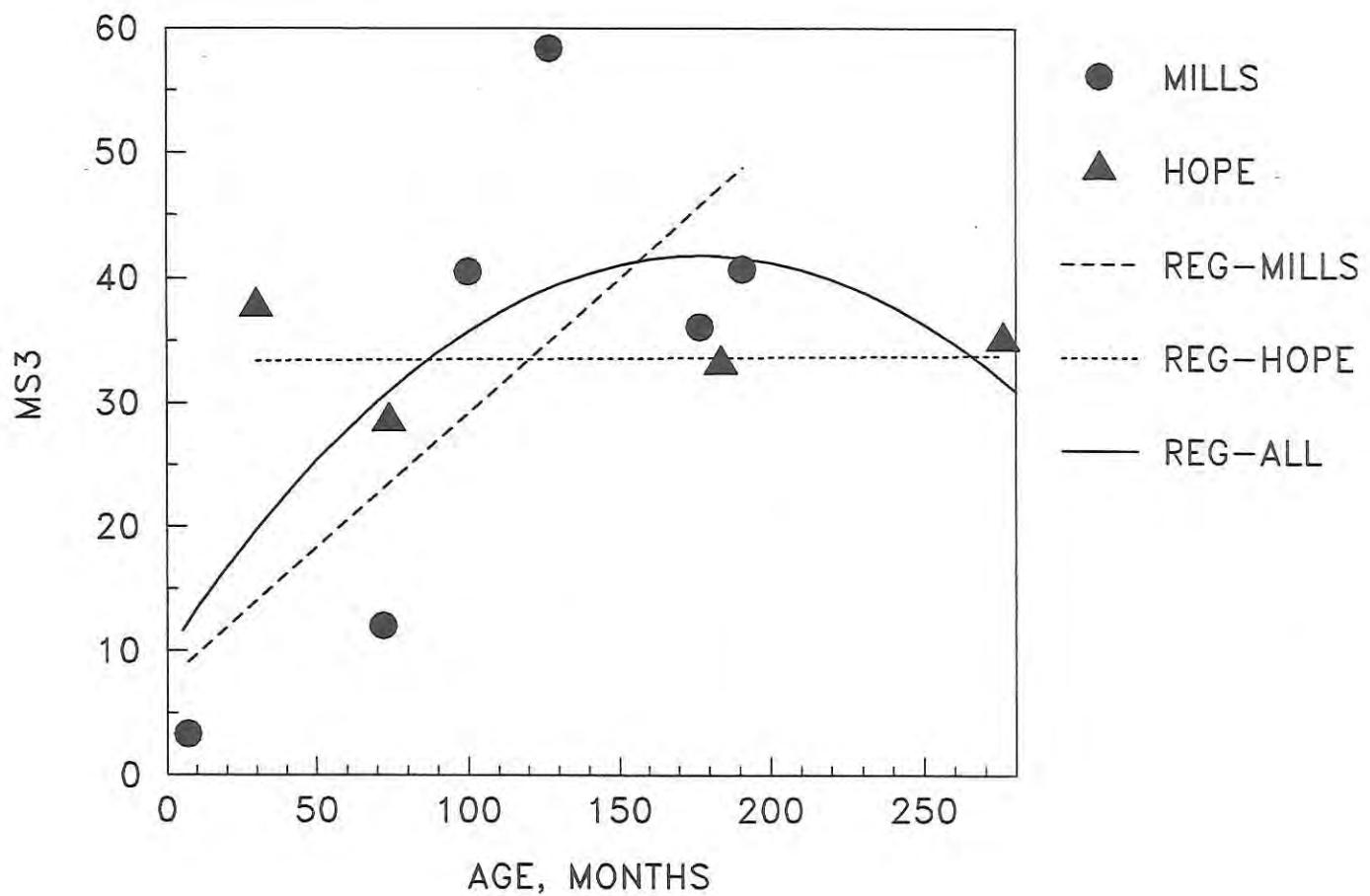


Figure 12. Mass Spectral parameter MS3 vs age of the parachute. Symbols same as in Fig. 4.

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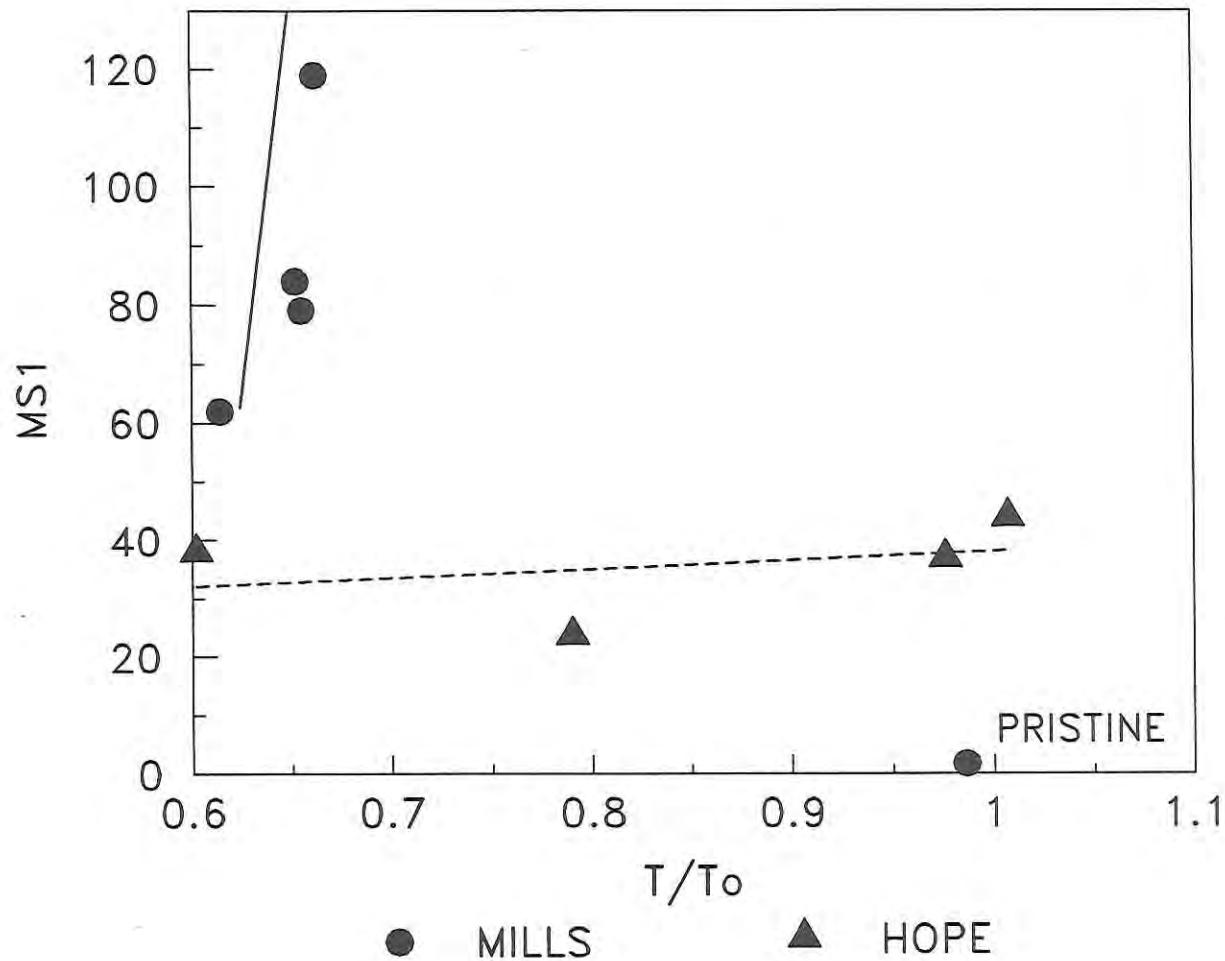


Figure 13. Mass Spectral parameter $MS1$ vs reduced tensile strength. Symbols same as in Fig. 4.

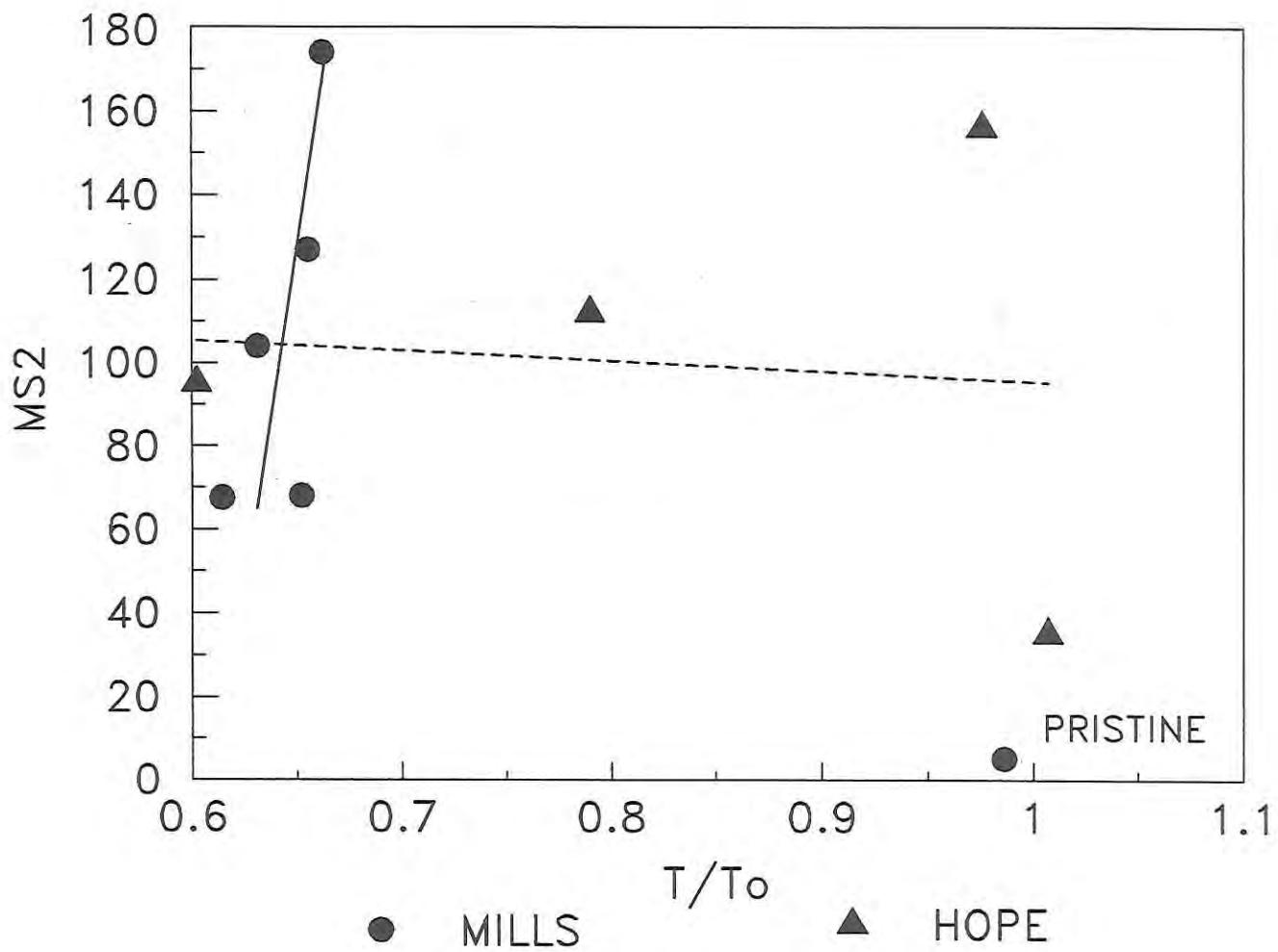


Figure 14. Mass Spectral parameter MS2 vs reduced tensile strength. Symbols same as in Fig. 4.

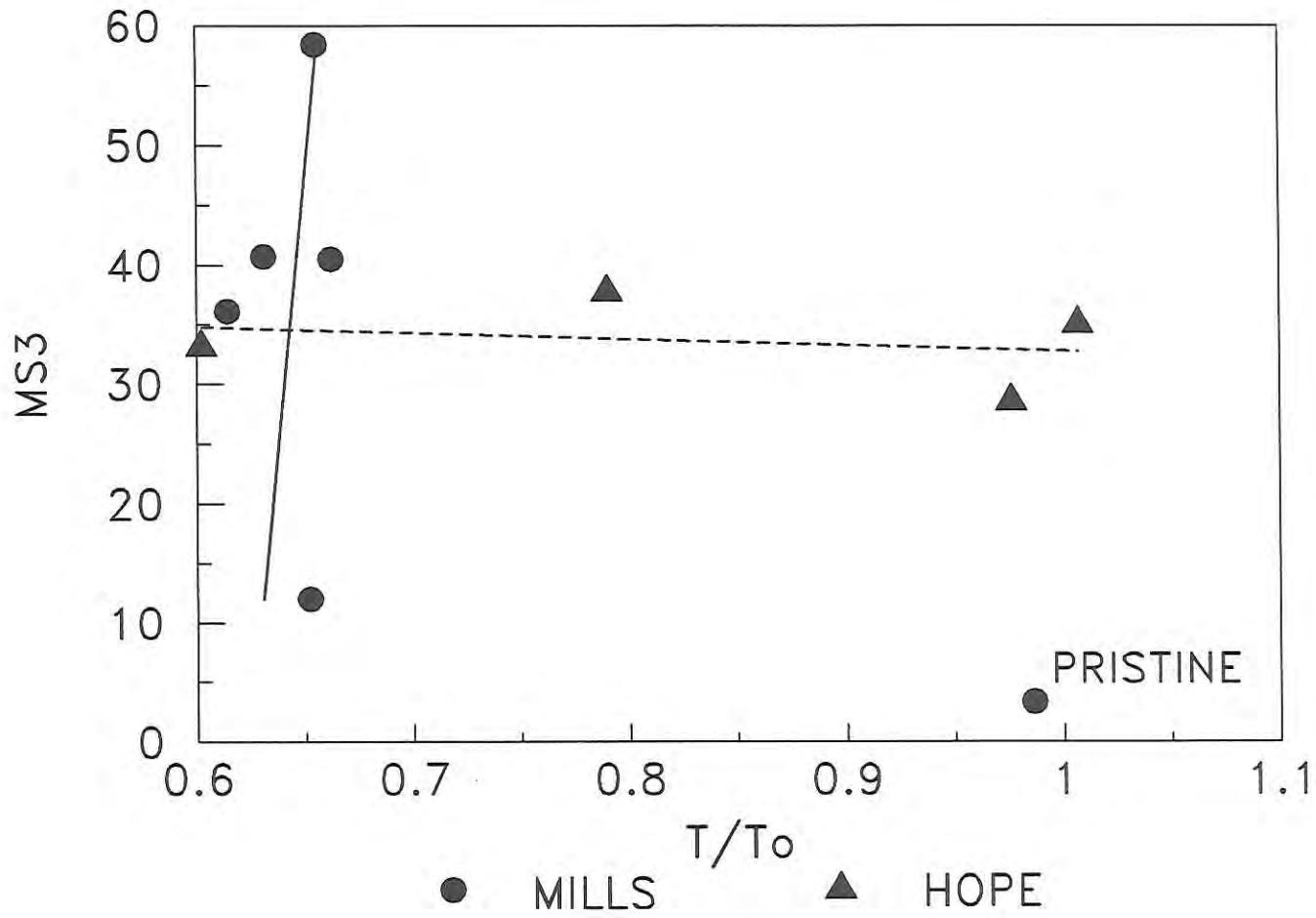


Figure 15. Mass Spectral parameter $MS3$ vs reduced tensile strength. Symbols same as in Fig. 4.

range of 0.1 to 0.4 mg/mL of trifluoroethanol. The optical absorption spectra of the nylon solution were determined over the wavelength range of 190 to 450 nm using a Perkin Elmer spectrophotometer (Model No. Lambda 4C, with a 7700 data processor). Trifluoroethanol was used as the blank.

Spectra comparing 74- and 288-month old parachute suspension cord are shown in Fig. 16; data for both core and sheath are included. Figure 17 compares data for 39- and 177-month old cord. No significant differences are seen in either figure for either the core strands or for the sheath.

DISCUSSION

GENERAL: Ideally, to study the effects of aging, it would be best if sufficient nylon material could be placed into storage, under various simulated climatic conditions, and evaluated each year for a period of 15 to 20 years. This was obviously not possible within the scope of this project. Only one set of data was found where such a study was made (24); this study extended over a 9-year period. The data are included in Fig. 1, even though they were obtained on canopy fabric, because the information represents the only controlled storage data available that includes periodic evaluations. The variation in tensile strength from year to year scattered considerably but the overall trend agrees well with other data and the conclusions drawn from the data on used parachutes.

A long-term storage study was initiated at Natick in the late 1950's, but lack of funding prevented yearly analyses and the only data obtained on these materials came after eight years of storage (16). The results of this limited study proved very useful in interpreting and evaluating test

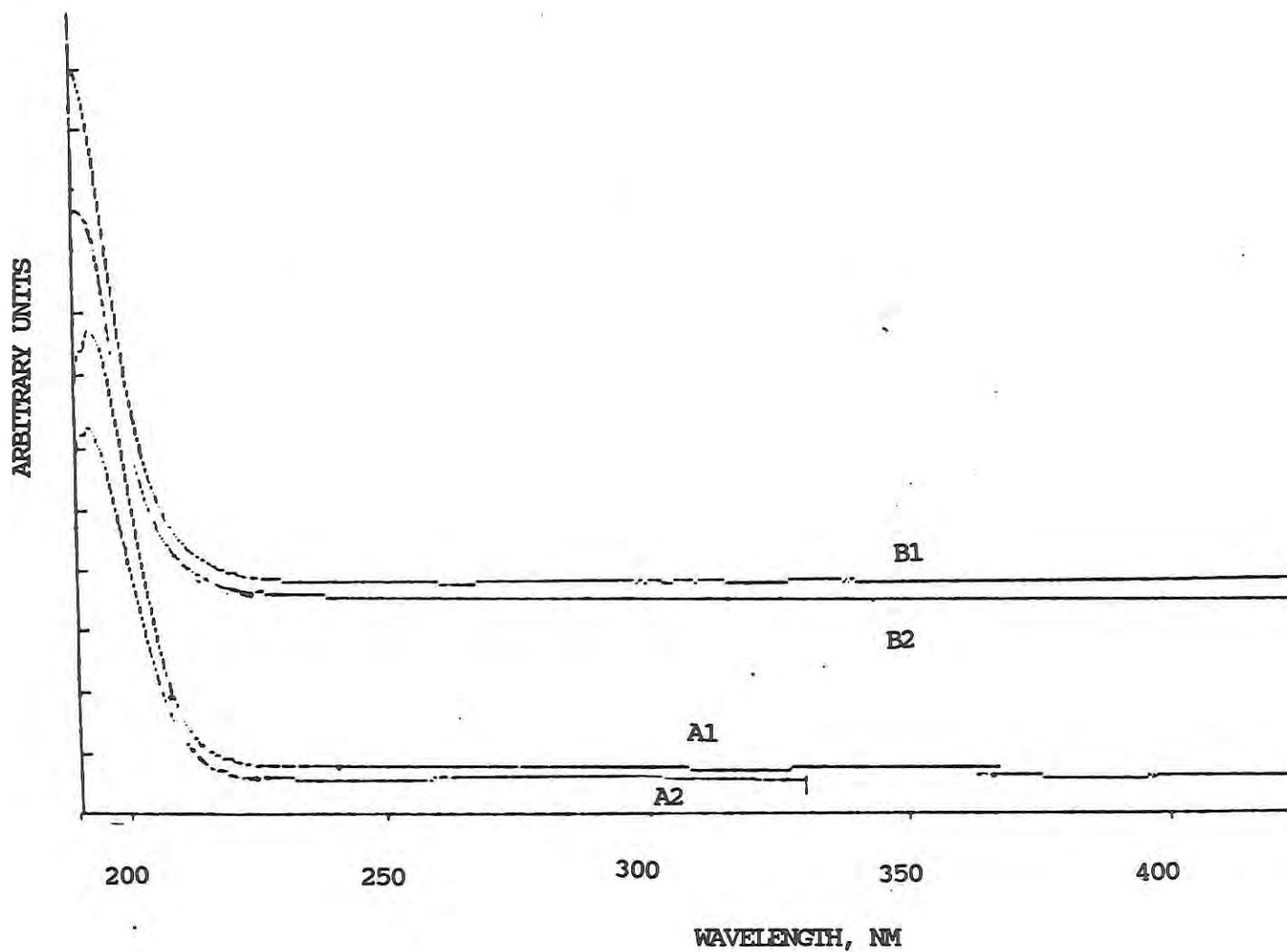


Figure 16. UV/vis spectra for 74 month old (A) and 228 month old (B) parachute cord. Spectra for both the core (1) and sheath (2) are shown.

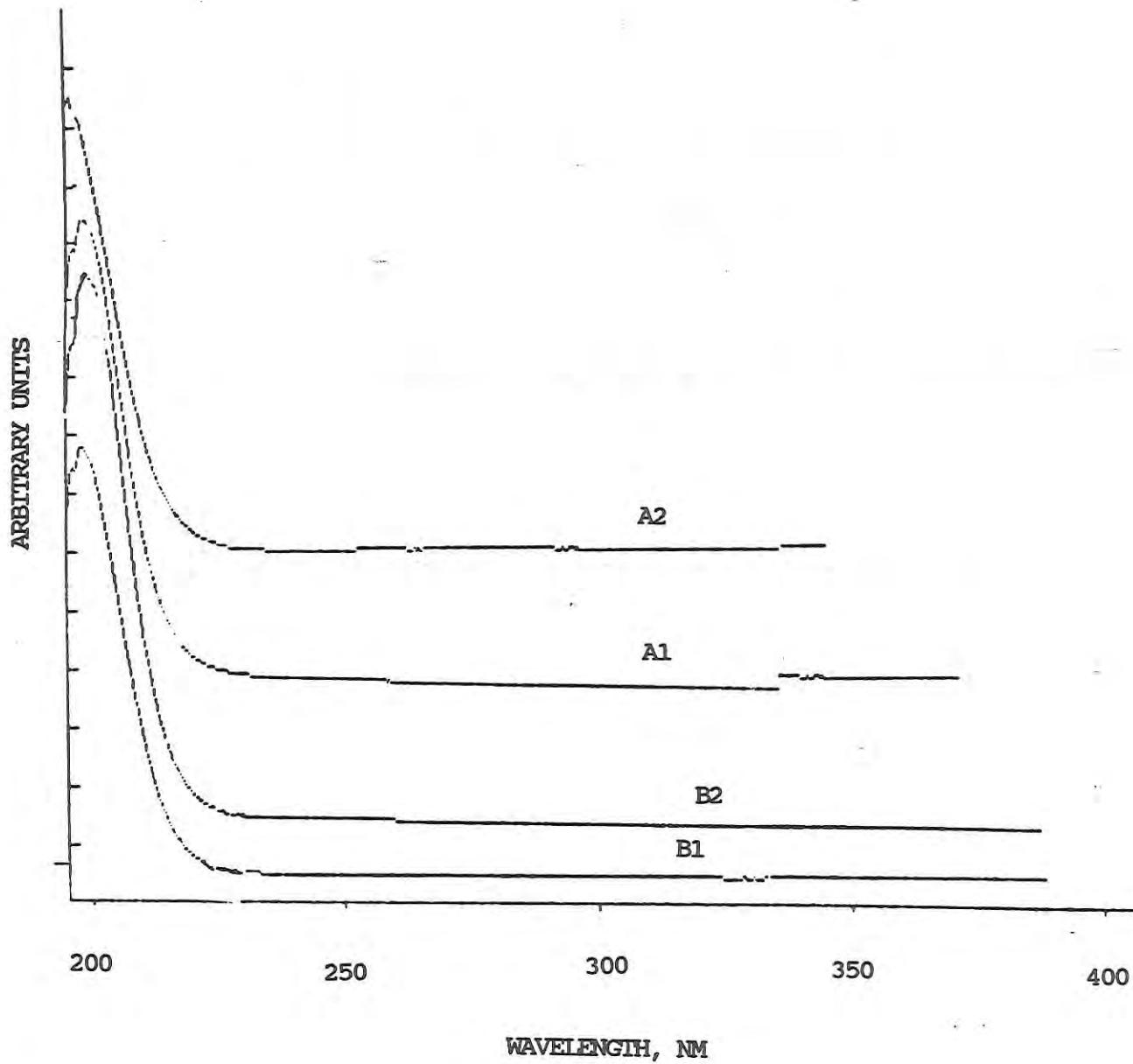


Figure 17. UV/vis spectra for 39 month old (A) and 177 month old (B) parachute cord. Spectra for both the core (1) and the sheath (2) are shown.

data found in the literature. This 8-year study provided data on parachutes stored under four climatic conditions, tropic, desert, temperate summer and arctic. The tropic environment proved to be the best storage condition for maintaining the tensile strength of the nylon cord. The high humidity apparently provided protection against oxidation at the normal tropic temperatures.

In contrast, studies in which high temperature accelerated aging was used (4,5), show that high humidity accelerates degradation of the nylon. It is clear that the effect of humidity on the degradation of nylon cannot be determined in studies involving high temperature accelerated aging. Even in desert conditions, the worst case, the degradation rate was similar to that deduced from all other measures (Fig. 1).

ACCELERATED AGING: Since long-term storage studies (15 to 20 years) are beyond the reach of most research efforts, the use of accelerated aging has played a significant role in studying the degradation of nylon 66. Work at the Sandia Labs. has made extensive use of elevated temperatures to accelerate the aging of nylon. Many of the temperatures used were above the glass transition temperature (T_g) of the nylon. It has been reported (10) that reaction dynamics are different above and below T_g and that reaction rates determined at temperatures above T_g cannot be extrapolated to ambient temperature. The studies on the effect of humidity discussed above provide one example. The Sandia research, which showed that high humidity accelerates degradation, used temperatures above T_g ; early (1968) in-house work shows that at ambient storage temperatures, high humidity (tropic environment) retards degradation. This raises the question of the effectiveness of using high temperature

accelerated aging to study any of the various factors that cause degradation of nylon. High temperature aging can not be used to study degradation mechanisms unless the reaction dynamics of the factors under consideration are well understood.

Researchers at the Materials Research Laboratory in Australia have also made extensive use of high temperature accelerated aging. All temperatures used in their work were near or below T_g . Good correlations were obtained between the length of time aged at an elevated temperature and (a) the disappearance of amine end groups and (b) the concentration of carboxyl groups. Since these chemical changes are due primarily to chain scissions, which in turn reduce the tensile strength, a good correlation was obtained between the time aged at elevated temperature and the tensile strength. Assuming the reactions that produce chain scissions and the reduction of tensile strength are first order, an Arrhenius plot allows extrapolation of the high temperature degradation rates to ambient temperatures. Thus the degradation rate (tensile strength loss) for nylon stored at ambient temperature can be estimated from test data obtained on nylon aged at elevated temperatures. However, the assumption that the sum of all reactions occurring in the nylon is the same as a single first-order reaction may not always be valid. For example, if an UV inhibitor or antioxidant is present, the initial degradation rate would be suppressed and only after the inhibitor or antioxidant is depleted would the true degradation rate appear. Such changes in the reaction rates could not be detected using accelerated aging. Also, if several first-order degradative mechanisms are working in

concert, it is unlikely that the result of their actions will remain first order. Elevated temperatures may produce additional degradation through changes in structure (29), which would also limit the range of first-order behavior.

DATA FROM USED PARACHUTES: With the above limitations on accelerated aging and the realization that long-term storage was far beyond the scope of this study, the only course left was a thorough study of the literature, including old data, as long as it was obtained on nylon 66. The literature search provided only two studies where nylon 66 was subjected to controlled storage conditions designed to simulate known storage conditions for military parachutes. One study done in-house was very limited; it contained only one set of data taken after eight years of storage. The second study done in India provides annual data for a nine-year period on one set of nylon 66 canopy material. For this study the tensile strength in both the warp and fill directions was given. The remaining data found in the literature were obtained on parachutes used by the Army or the U.S. Forestry Service. These used parachutes provide the bulk of the information contained in this study. The main drawback of the data on used parachutes is that the original strength of the nylon, either the cord or the canopy material, is not known. Undoubtedly the strength was somewhat above the minimum required by the specification, which for the parachute suspension cords represented in Fig. 1 is 400 lb, but how much above is uncertain and probably varies from lot to lot. We have arbitrarily set the initial strength, T_0 , at 5% above the minimum required by the specification, i.e., $T_0=420$ lb (190.5 kg). This

arbitrary choice of T_0 will affect the total amount of degradation shown in Fig. 1 but will not affect relative values and will not change conclusions about the rate of degradation due to age. Changing the value of T_0 simply shifts all data points (or the vertical axis) up or down.

The problem then reduces to extracting the effect of aging from the combined effect of age and use. It is fortunate that some of the data in Fig. 1, the parachutes from the U.S. Forestry Service, come with a complete history of the parachute, in particular the number of times the parachute has been jumped. Working with these data it is possible to ascertain the effect of jumping on the tensile strength of the parachute cord. Linear, quadratic and multiple linear regressions were applied to the data from the forestry parachutes as described in the previous section. It is clear that the number of jumps is responsible for most of the changes in the tensile strength of the parachute suspension cords. For the quadratic curve the correlation coefficient is 0.85, while for the multiple linear regression where age is included as the second independent variable the coefficient is only 0.80 (number of jumps is the first independent variable). Thus, a better prediction of the tensile strength is possible using only the number of jumps than when the number of jumps and age are combined. This is also shown in Fig. 3 where the predicted tensile strength is plotted against the actual values. The predicted values are determined using in one case the quadratic fit and in the second set of data the multiple regression equation. There is no significant difference between the two sets of data, showing again that the number of jumps a parachute has experienced is the primary factor governing its cords' tensile strength.

The effect of repeated strain cycles, or simulated jumps where parachute suspension cord was subjected to sudden impact drop tests, was recently studied in-house (21). This study showed that even under clean jump conditions the tensile strength decreased with the number of jumps until about 30 jumps had occurred after which the tensile strength remained nearly constant for up to 300 cycles. The decrease in strength for the first 30 cycles (jumps) was about 7 %. When exposed to sand/grit between cycles the effect of mechanical work-in was much greater; a loss of about 40 % occurred after 40 cycles. For actual jump conditions where the cord may be exposed to grit, UV absorption, moisture, etc., it is reasonable to expect the effect of mechanical work-in to be as large as for the artificially contaminated samples. From Fig. 1 it appears that this mechanical work-in causes a 30 to 35% decrease in the tensile strength.

Considering all the data in Fig. 1 and the results of the in-house study (21) it seems reasonable to assume that the sharp decrease in tensile strength that occurs over the first five years is due to mechanical work-in. That is, in most cases it takes at least five years from date of manufacture for a parachute to reach the 30-40 jump level required to complete its mechanical work-in. In fact, the many parachutes that fall far above the worst case curve may not have reached the end of their work-in period (there is no record of the number of jumps they have experienced) and therefore appear stronger when tested on an Instron than a fully worked parachute of comparable age.

If a 30 - 35% decrease in tensile strength is assigned to mechanical work-in and this decrease is assumed to occur over the first five years

after manufacture, as Fig. 1 suggests, then the small decrease in tensile strength (about 5%) from year 5 to year 20 can be attributed to age.

Following this hypothesis, age alone causes about a 0.3% per year decrease in the tensile strength of parachute suspension cord. This is slightly less than the 0.75% per year estimated from the accelerated storage data.

The data on stored canopy material show about a 1% per year decrease in tensile strength, which is similar to the suspension cord material stored under desert conditions. The data for parachute suspension cord stored at temperate summer conditions show about a 0.5% per year decrease while the suspension cord stored under tropical and arctic conditions show almost no change in tensile strength after eight years. Once the concept of mechanical work-in is accepted, the data in Fig. 1 are quite easily explained and the effect of age is easily extracted from the combined effect of age and use (number of jumps). The best estimate of the effect of age on the degradation (loss of tensile strength) of nylon 66 is that age causes a tensile strength loss of about 0.5% per year. Whatever the degradation rate due to age, it is clear that use, primarily the number of jumps, is by far the most significant factor in the degradation of nylon 66.

FLUORESCENCE MEASUREMENTS: As stated in the previous section, other researchers (1,2) have shown that a strong correlation exists between the tensile strength of nylon suspension cord and its UV absorption characteristics, primarily the absorption intensity at 245 nm. This work used accelerated (high temperature) aging to produce the changes in the nylon. In these studies, temperatures as high as 150°C, which is far above the glass transition temperature of 107°C, were used.

One goal of the present study was to determine whether or not optical measures could be used to monitor the tensile strength of parachutes stored at normal warehouse conditions. The used parachutes from the "Just cause" exercise provided ideal samples to address this problem since the age of these parachutes ranged from 3 to 15 years. Several parachutes selected from this group were tested as described in the previous section and the results plotted in Figs. 4 to 9. When the fluorescence parameters are plotted against the age of the parachute, only the ratio of the emitted intensity at the wavelength of maximum emission to the intensity of the scattered light (Fig. 4), shows any correlation. For this parameter, when age is in months, the best least squares fit is given by the quadratic curve

$$I_m/I_s = 3.13E^{-2} - 1.77E^{-4}(\text{AGE}) + 1.97E^{-6}(\text{AGE})^2$$

with a correlation coefficient of 0.95. The two remaining fluorescence parameters plotted in Figs. 5 and 6 show no correlation between the fluorescence measure and the age of the parachute; R^2 values are 0.08 and 0.05 respectively. In Figs. 7, 8 and 9 the fluorescence parameters are plotted against the tensile strength of the parachute; none of the parameters shows any correlation. The fluorescence data were obtained on parachute suspension cord from three different manufacturers; seven parachutes used suspension cord made by Miltex, five used suspension cord made by Hope and one used suspension cord made by Continental.

When considering only the parachutes from a single cordage manufacturer, a pattern begins to emerge in plots where reduced tensile

strength is the abscissa. If the data obtained on pristine cord (one of the samples manufactured by Miltex) is ignored, then the Miltex samples show a considerable change in fluorescence for a very small change in the tensile strength, while the cord manufactured by Hope shows very little change in fluorescence over a wide range of tensile strengths. This suggests that the fluorescence-producing species is not inherent in the nylon 66, or its breakdown products, but is instead coming from a manufacturer-added material, such as the lubricant used in the yarn-spinning process. The limited number of samples for which fluorescence data were obtained are not sufficient to prove the above hypothesis. Even after separating the data according to manufacturer, considerable variation exists, particularly when including the pristine suspension cord manufactured by Miltex. However, this hypothesis is consistent with other measurements as shown in the next section.

GC/MS ANALYSIS: Mass spectral analyses were performed on most of the samples used for the fluorescence measurements. As described in the data analysis section, the three major peaks were identified and used as indices for comparing the samples; the results are shown in Figs. 10 through 15. Figs. 10, 11 and 12 show the three indices plotted against the age of the parachute. When the data from all samples (cordage manufactured by Miltex and Hope) are considered there is no correlation, but when the data are separated by manufacturer, the trends shown by the fluorescence data, Figs. 8 and 9, appear also in the mass spectral data. The cordage samples manufactured by Miltex show large changes in the mass spectral measures for little change in the tensile strength while the samples manufactured by Hope show almost no change in the mass spectral

data for large changes in the tensile strength. These trends are more pronounced in Figs. 13, 14, and 15 where the mass spectral indices are plotted against the tensile strength of the suspension cords. Here the trends are almost identical to those shown by the fluorescence data of Figs. 8 and 9.

The peaks used as indices for the mass spectral analyses come from high molecular weight materials and are not believed to be inherent in the nylon 66 itself or its breakdown products. It is thought that the material producing these peaks comes from traces of the lubricants used in the spinning of the threads. The mass spectral data did not reveal any products that were clearly breakdown products of the nylon. Since the lubricants used are manufacturer specific, the sensitivity of the mass spectral data to manufacturer is readily explained. If these lubricants contain fluorescent species, then the sensitivity of the fluorescence data to manufacturer is also readily explained. It is clear from these studies that neither fluorescence measures nor mass spectral data can be used to predict the tensile strength of new or used parachute suspension cords that have been stored at normal ambient temperatures, particularly if the parachutes are made by more than one manufacturer.

UV/VIS SPECTRA: UV/vis spectra were obtained on all 13 parachute suspension cord for which fluorescence data were taken. Data from individual runs were compared by matching an "old" cord with a relatively "new" cord to see if any differences could be observed. Figures 16 and 17 are typical of the many comparisons made. There is no significant difference in the UV/vis spectra of old and new parachute suspension cord. Also, no manufacturer-dependent differences could be detected in

the uv/vis data. The UV/vis data fully support the conclusion that the tensile strength of parachute suspension cord changes very little with age.

ANALYSIS AND CONCLUSIONS

It is clear that the ideal method to determine the effect of age on the degradation of nylon 66 would require the evaluation of the pristine material and placement of sufficient pristine material into controlled storage, using all storage conditions that are of interest, to permit testing at least once a year for 12 to 15 years minimum. Such an undertaking requires an extreme commitment and, as in one study reported here, will likely fail because of lack of funds or interest and perhaps both. The one study that did run for 9 years showed much scatter that might be attributed to changes in the personnel preparing and evaluating the test specimens throughout the long period of the study. Thus, even the "ideal" study is not without problems.

The use of accelerated aging reduces the time scale of the study considerably but may generate conclusions that are not universally valid. The effect of moisture on the degradation of nylon is such an example; at high temperatures it tends to accelerate degradation while at ambient temperatures it tends to protect the nylon. Normally stored used parachutes offer the only other source of data on the degradation of nylon. Unfortunately, at present there is not enough information maintained on used parachutes, i.e., number of jumps, average load, ground conditions, etc. to permit an accurate assessment of the contribution of

use to the overall degradation. Also, at present the initial conditions of the material from which the parachutes were made is not known. Thus, as in the present study, an estimate of the initial strength of the parachute must be made. If the physical properties of the parachute material when it was new were known, along with all the jump conditions, the effect of all factors, particularly age, could be readily and accurately determined. When the limitations of accelerated aging and the commitment required of long-term storage studies are considered, the only reasonable alternative lies in the use of data obtained on used parachutes.

It is essential that the physical properties of the parachute cord material in its pristine condition be available throughout the life of the parachute and that the use history including the number of jumps, average load of each jump and the ground conditions at jump locations be maintained as part of the parachute record. This will permit a more accurate assessment of the aging of nylon than was possible in this present report.

The data obtained from the literature and reported here does give a reasonable indication of the degradation rate of nylon parachute material as a function of the age of the parachute. Assumptions were made that reduce the accuracy in determining the absolute amount of degradation due to the combination of age and use. The effect of the number of jumps was investigated using only a limited number of test samples. If the jump histories of more parachutes were known, a better estimate of the effect of the number of jumps could be made. The effect of jump load and of the ground conditions at the landing site were not considered since no data

on these factors were found in the literature. In spite of the above limitations, the present report clearly shows that jump history, at least the number of jumps, is the major factor causing a loss in the tensile strength of the parachute suspension cord. This was clearly shown using the data on parachutes obtained from the U.S. Forestry Service.

A reasonable estimate of the effect of jump history then allows an equally reasonable estimate of the loss in tensile strength due to age alone.

From the present data it seems reasonable to claim that mechanical work-in (up to 30-40 jumps) accounts for a 30 to 35% loss in tensile strength during the first five years of the life of the parachute and that age causes a loss in tensile strength of about 0.5% per year.

In-house studies on the effect of strain cycling, i.e. number of jumps, in both clean laboratory environments and in controlled field conditions (different sand/grit treatments) clearly show that there is a period of mechanical work-in where successive cycles (jumps) cause a decrease in the tensile strength of the cord up to as many as 30 to 40 cycles. In the clean environment the decrease may be less than 10% but in the more realistic conditions the decrease is as much as 40%. These studies provide a good explanation of the data plotted in Fig. 1 and help determine the effect of age.

Regarding the effect of age, it is apparent from Fig. 1 that when the effect of the number of jumps is subtracted from the overall loss in tensile strength, the remaining strength loss amounts to only about 0.5% per year. At present this is the best estimate of the effect of age on the degradation of parachutes.

The use of high temperature accelerated aging to study the degradation of nylon appears to have several serious drawbacks, especially when factors that cause the degradation are to be investigated. In studying the effect of moisture, high temperature aging shows that moisture increases the rate of degradation while one study done at ambient temperatures found that the high moisture condition (tropic environment) provided the best storage condition. High temperature aging should not be used to study the effect of various degradative factors unless the reaction kinetics of the particular factor is well known.

Fluorescence measures correlate well with the tensile strength of parachute suspension cord when the cord has been artificially aged at high temperatures. In the present study where only normally aged material (used parachutes) has been evaluated, there was no correlation between any of three fluorescence measures and the tensile strength of the parachute suspension cord when all parachutes evaluated (three cordage manufacturers) were considered. Trends were apparent when the cordage from each manufacturer was considered separately. This suggests that the fluorescing species is a manufacturer-specific additive or process and not an inherent part of the nylon 66.

Chemical analysis of the parachute suspension cords using a mass spectrometer revealed the existence of several high molecular weight materials, which appeared to be from traces of a lubricant required in the spinning process. When studying the data from a single manufacturer, the trends observed are very similar to those found in the fluorescence data. The materials found are manufacturer specific, i.e., from use of different lubricants. It seems possible that the materials identified by mass

spectral analysis are also responsible for the fluorescence. No products were found that provided evidence of a breakdown of the nylon.

FUTURE CONSIDERATIONS/RECOMMENDATIONS

The weak link in the present effort is the lack of data regarding the suspension cord strength at the time the cord was manufactured. Only the specified minimum strength was known and an arbitrarily chosen value 5% higher than this was taken as the strength of the cord in its pristine condition. Known values of initial cord strength/elongation would permit future researchers to make a more accurate assessment of nylon degradation.

Secondly, since the number of jumps is known to have an adverse effect on parachute suspension cord strength (particularly for the first few jumps), data on the number of jumps would allow future researchers to remove this factor from aging studies. Also, a more accurate assessment of the effect of jump history could be made.

Thirdly, keeping records of jump conditions such as load (static or dynamic), terrain, etc. would help reduce or explain differences/scatter in any data to be analyzed in the future. Even without future research, recording/monitoring these factors will help tremendously in assessing the serviceability of any parachute being readied for use.

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